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Study of the Electronic Structure of Molecules. XVI. Analysis of the Formation of the Methane Molecule in the Hartree–Fock Model

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Abstract: The energy of formation for the methane molecule (in the Hartree–Fock approximation) is analyzed by (1) building up the electronic configuration starting from the nuclear field and adding one pair of electrons at a time; (2) by variation of the C–H distances; (3) by removing a single electron from each orbital (single ionization). The energy and electronic densities for CH_4^{8+}, CH_4^{6+}, CH_4^{4+}, CH_4^{2+}, CH_4^+, and CH_4 are discussed using two methods. The first technique uses Hartree–Fock atomic data and a very simple physical model (requiring essentially no computations). With this method, the total energies and the orbital energies of CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} are computed to about the same accuracy as obtained from the Hartree–Fock molecular computations (the second technique). The Hartree–Fock energies are analyzed with the bond energy analysis technique, and the Hartree–Fock densities are analyzed with the electron population analysis technique. The study of the ionization potentials of a single electron (from each of the occupied orbitals) brings about a clear indication of the large amount of reorganization which follows ionization. This effect was pointed out in paper VI of this series for valency electron; it is now stressed for inner shell electrons. It is noted that the 100% agreement between the computed and the experimental ionization potential for the inner shell indicates that the correlation corrections are affected by the rearrangement to about the same per cent as the Hartree–Fock energies. A discussion on the hybridization for methane would predict (in a Hartree–Fock model) a s^2p^2 hybridization; however, mainly because of charge-transfer effects, the hybridization is about $s^{1.5}p^{2.5}$; clearly, the hybridization is a function of the C–H distance and of the degree of ionization of the species (and these effects are discussed).

The present status of molecular computations has reached the point where, for relatively small molecules, one can routinely obtain Hartree–Fock type wave functions and energies. With some difficulty, one can obtain 50–60% of the correlation correction both in the wave function and energy. With considerable difficulty, one can obtain 85–95% of the correlation correction both in the wave function and energy. Exact wave functions and energies are not yet within reach, if by exact we mean a wave function to about four decimals in any point of the space (excluding the small volume near the nucleus) and about four decimals (in atomic units) in the total energy.

Because of the special position the Hartree–Fock model has in the conceptual understanding of the electronic structure of molecules, and, because of the ease in obtaining Hartree–Fock functions, we shall examine in fuller detail the mechanism of molecular formation implicit in the Hartree–Fock model. The aim of this work is not the presentation of Hartree–Fock data for a given molecule, *but a study of these data*, in order to present a simple physical model attempting to explain (for a given example) why the Hartree–Fock values obtained by the Hartree–Fock machinery are as they are.

In particular, we shall focus our attention on the total energy and orbital energies, and we shall attempt to connect molecular Hartree–Fock data with atomic Hartree–Fock data. It is noted that, despite the emphasis placed on the orbital energies for estimates of ionization potentials and other electronic excitation processes, given a molecule (of specified geometry) it is still not too easy to predict the orbital energies (without elaborate computations requiring electronic computers) with sufficient accuracy, so as to allow comparison with the orbital energies of a similar molecule (or of the same molecule at a different geometry).

In short, we would like to examine Hartree–Fock data and attempt to explain the computational results obtained from elaborate computations with simple physical arguments obtained following the spirit of the model. To partially reach our aim, we shall build up the molecular electronic structure by adding a pair of electrons at a time, we shall vary the molecular geometry, and, finally, we shall ionize the molecule by creating electronic holes. (It is noted that as a by-product we shall obtain data of value in themselves.)

The example chosen is the methane molecule. The reason for this choice is that the Hartree–Fock model works fairly well for this molecule. It predicts the geometry with sufficient accuracy [tetrahedral structure and a C–H bond length of 2.045 au (experimentally CH_4 has tetrahedral geometry and a C–H bond length of 2.0665 au)] and a binding energy of about 80% of the experimental (the experimental binding energy is 0.668 au and the computed binding is 0.528 au).

Since the atomization products of CH_4 are a carbon atom in the ^3P state and four hydrogens in the ^2S state, the formation of the methane ground state (a singlet state) requires the creation of four new electron pairs in the molecule (the four bonds). In general, the Hartree–Fock error is around 1.5 ± 0.5 eV per pair; for methane, the computed Hartree–Fock binding energy is in error by about 0.140 au or about 1 eV per pair. Thus, the methane molecule is a rather typical example of what the Hartree–Fock model can do.

We have attempted no optimization of the basis set, since we have used one of the optimized basis sets derived by van Duijenevelt[1] in his careful study of an optimal basis set for methane. The basis set is discussed in the Appendix.

We shall first consider a set of four protons and one carbon nucleus, arranged so as to conform to the molecular geometry of the methane molecule in the ground state. In this field, we shall introduce the electron pairs, one at a time. Thus, we consider CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}. (This is an example of the so-called "building up principle.")

Building Up of Methane. The First Six Electrons in the Field of Four Protons and a Carbon Nucleus at Constant Geometry

We start with the strongly repulsive field of four protons and a carbon nucleus at the CH_4 equilibrium geometry (the repulsion is 13.391887 au) and we add to it two electrons at a time, until we obtain CH_4^{4+}.

We know that the first six electrons will be mainly atomic in character and, therefore, will surround mainly the carbon nucleus with a small amount of electronic charges (if any) at the protons. We start the building-up study *by attempting to predict* some of the energetic characteristics of CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}. Making use of atomic computations previously reported[2] for the carbon atom and its ions, we shall compare the predictions with Hartree–Fock computations on the methane ions. We assume that the total energy, E, of the ions is obtained by adding the energy of C^{4+}, C^{2+}, and C to the nuclear-nuclear repulsion (E_{nn}) and the point charge electrostatic interaction between the protons and the electrons. Thus, we write for the total energy, E, of the ions

$$E(CH_4^{8+}) = E(C^{4+}) + E_{nn} - 4(2/R(CH)) = -32.3611 + 13.3919 - 3.8712 = -22.8404$$

$$E(CH_4^{6+}) = E(C^{2+}) + E_{nn} - 4(4/R(CH)) = -36.4085 + 13.3919 - 7.7424 = -30.7590$$

$$E(CH_4^{4+}) = E(C) + E_{nn} - 4(6/R(CH)) = -37.5495 + 13.3919 - 11.6136 = -35.7712$$

It is noted that the distances $R(HH)$ and $R(CH)$ are 3.374569 and 2.0665 au, respectively.

Having estimated the total energy, we now also estimate the orbital energies, ϵ, and the one-electron energies, h, for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}.

We start with CH_4^{8+}. The one-electron energy, h_1, for CH_4^{8+} is equal to the one-electron energy, $h_1(C^{4+})$, for the carbon center plus four times the nuclear–electron attraction between one 1s electron at the carbon and the proton (*i.e.*, $-4(1/R(CH)) = -1.9356$ au). Thus, we obtain

$$h_1(CH_4^{8+}) = h_1(C^{4+}) - 4/R(CH) = -17.9444 - 1.9356 = -19.8800 \text{ au}$$

and since

$$E(CH_4^{8+}) = \epsilon_1(CH_4^{8+}) + 2h_1(CH_4^{8+}) - E_{nn}$$

we obtain

$$\epsilon_1(CH_4^{8+}) = -22.8404 + 19.880 - 13.3919 = -16.3523 \text{ au}$$

We now consider the CH_4^{6+} ion. The estimate for the one-electron energies $h_1(CH_4^{6+})$ and $h_2(CH_4^{6+})$ and for the orbital energies $\epsilon_1(CH_4^{6+})$ and $\epsilon_2(CH_4^{6+})$ are approximated as follows. Since the overall electronic densities in CH_4^{6+} and C^{2+} are closely related, we assume (1) that $e_i(CH_4^{n+}) \cong e_i(C^{(n-4)+})$ and (2) the fraction of h_1 and h_2 in CH_4^{6+} that expresses the kinetic energy and the energy of attraction between the electrons and the carbon nucleus is equal to h_1 (and h_2) in the C^{2+} ion. Therefore, we can write

$$h_1(CH_4^{6+}) \cong h_1(C^{2+}) - 4/R(CH) = -17.9444 - 1.9356 = -19.8800 \text{ au}$$

$$h_2(CH_4^{6+}) \cong h_2(C^{2+}) - 4/R(CH) = -4.1194 - 1.9356 = -6.0550 \text{ au}$$

$$\epsilon_1(CH_4^{6+}) \cong h_1(CH_4^{6+}) + e_1(C^{2+}) = -19.8800 + 5.2939 = -14.5861 \text{ au}$$

$$\epsilon_2(CH_4^{6+}) \cong h_2(CH_4^{6+}) + e_2(C^{2+}) = -6.0550 + 2.4254 = -3.6296 \text{ au}$$

Finally, we consider the CH_4^{4+} ion. The estimates of the h's and ϵ's for the CH_4^{4+} ion are obtained by use of the same assumptions used for CH_4^{6+}). (We do expect, however, that the assumption will be progressively poorer in passing from CH_4^{8+}, CH_4^{6+}, to CH_4^{4+}, since more and more electronic charge is in the vicinity of the protons.) For the CH_4^{4+} ion, we obtain $h_1 = -19.8800$ au, $h_2 = -6.0550$ au, $h_3 = -4.9810$ au and $\epsilon_1 = -13.3267$ au, $\epsilon_2 = -2.6750$ au, $\epsilon_3 = -2.2454$ au, respectively.

The model above used is very simple and the agreement with the computed Hartree–Fock total electronic energy is 100, 99.97, and 99.96% for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}, respectively, and between 100 and 96% for the orbital energies; this can be seen from the data reported in Table I for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}.

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(1) F. van Duijenevelt, Department of Chemistry, University of Utrecht, to be published; private communications.

(2) E. Clementi, *IBM J. Res. Develop., Suppl.*, 9, 2 (1965).

Table I. Comparison of CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} with the Lowest Singlet S for C^{4+}, C^{2+}, and C Ions and Atoms (in au)

Energy	$C^{4+}(^1S)$	CH_4^{8+}	$C^{2+}(^1S)$	CH_4^{6+}	$C(^1S)$	CH_4^{4+}
E, total energy	−32.3611	−22.8404	−36.4085	−30.7675	−37.5495	−35.7559
E_{nn}, nucl–nucl repulsion		+13.3919		13.3919		13.3919
E_e, electronic energy	−32.3611	−36.2323	−36.4085	−44.1594	−37.5495	−49.1478
h_1, one-electron energy for ϕ_1	−17.9444	−19.8798	(−17.9444)	−19.8760	(−17.9444)	−19.8696
h_2, one-electron energy for ϕ_2			(−4.1194)	−6.0836	(−4.1194)	−5.8669
h_3, one-electron energy for ϕ_3					(−3.0454)	−5.5114
ϵ_1, orbital energy for ϕ_1	−14.4167	−16.3525	−12.6506	−14.5713	−11.3911	−13.1253
ϵ_2, orbital energy for ϕ_2			−1.6940	−3.6285	−0.7394	−2.5649
ϵ_3, orbital energy for ϕ_3					−0.3098	−2.2096
e_1, electronic repulsion for ϕ_1	3.5277	3.5274	5.2939	5.3046	6.5533	6.7443
e_2, electronic repulsion for ϕ_2			2.4254	2.4551	3.3800	3.6228
e_3, electronic repulsion for ϕ_3					2.7356	3.3019

Table II. ϕ_1 Bond Energy Analysis for Neutral and Ionized Methane (in au)

Energy	C^{4+}	CH_4^{8+}	CH_4^{6+}	CH_4^{4+}	CH_4^{2+}	CH_4
h_1	−17.9444	−19.8798	−19.8760	−19.8696	−19.8675	−19.8673
h_1(C)	−17.9444	−17.9314	−17.9231	−17.9012	−17.9056	−17.9043
h_1(CH)		−0.4868	−0.4878	−0.4893	−0.4899	−0.4901
h_1(CHH)		−0.0002	−0.0002	−0.0003	−0.0004	−0.0004
e_1	3.5274	3.5274	5.3047	6.7443	7.8240	8.6576
e_1(C)	3.5277	3.5239	5.6235	6.5163	6.3159	5.8175
e_1(CH)		0.0009	0.0836	0.0593	0.4346	0.8343
e_1(CHH)		0.0000	0.0002	0.0103	−0.0386	−0.0829
ϵ_1	−14.4167	−16.3225	−14.5713	−13.1253	−12.0435	−11.2097
ϵ_1(C)	−14.4167	−14.4075	−12.2996	−11.3939	−11.5897	−12.0868
ϵ_1(CH)		−0.4860	−0.5715	−0.4301	−0.0553	0.3442
ϵ_1(CHH)		−0.0002	−0.0024	−0.0106	−0.0388	−0.0833

In Table I (also given for comparison) are the Hartree–Fock values for C^{4+}, C^{2+}, and the C atom in the ^1S state.

We shall now add a few comments for each electron pair, using data obtained from the bond energy analysis[3–6] of the Hartree–Fock computations for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}.

The First Electron Pair. In Table II the bond energy analysis (BEA) formalism has been used to decompose the orbital energy, ϵ, the one-electron energy, h, and the electron–electron interaction, e, for the lowest pair. (We have added the corresponding data from CH_4^{2+} and CH_4, for completeness.) For CH_4^{8+}, CH_4^{6+}, and CH_4^{4+}, we see that the simple model previously used is adequate when compared with Hartree–Fock computations. A quantity of interest is e_1(CH); this quantity requires an electronic charge on both the carbon and protons. It is very small *but not zero* from CH_4^{8+} to CH_4^{6+}, then sharply increases for CH_4^{2+} (its value is 0.43 au) and for CH_4 (its value is 0.84 au). The increase is expected since in CH_4^{2+} (or CH_4) there are two electrons (or four) around the protons. The very small (but nonzero) repulsion for CH_4^{8+} (and CH_4^{6+} and CH_4^{4+}) is an indication that a small electronic charge is on the protons even for this very highly ionized molecule. We note that, in general, the electron population analysis for the 1s inner shell electrons of atoms in a molecule does not yield a population of 2.0000 e, but slightly less. The small value of e_1(CH) points out the existence of a small degree of delocalization. Is this a "real" effect or a consequence of the chosen basis set? We would like to propose that this effect is a manifestation of the need for polarization function (in the basis set) *for the inner shell electrons.* Polarization functions are customarily added only for valence electrons. However, the field exerted by the proton (and, in general, by the surrounding nuclei) on the 1s electrons is *very* strong (see h_1(CH) in Table II) and nonspherical. Thus, the 1s must be polarized. It is noted *that a very small polarization in the wave function for the 1s inner shell electrons corresponds to a very large energy effect.*

Another quantity of interest is ϵ_1. From the decomposition of ϵ_1 into ϵ_1(C) and ϵ_1(CH), we notice that the value of ~11.3 au is the carbon atom.[2] This supplies another indication that the numerical similarity of the orbital energies of inner shell in molecules and the corresponding inner shells in atoms should not be used to conclude that the inner shell electrons in an atom experience the same field as the one in a molecule.[7]

The Second Electron Pair. The energy decomposition for the second pair is given in Table III, where we decompose h_2, e_2, and ϵ_2 into one-, two-, three-, and

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(3) E. Clementi, *J. Chem. Phys.*, **46**, 3842 (1967).

(4) E. Clementi, *Int. J. Quantum Chem.*, **3**, 179 (1969).

(5) E. Clementi and W. von Niessen, *J. Chem. Phys.*, **54**, 521 (1970).

(6) E. Clementi and A. Routh, *Int. J. Quantum Chem.*, in press.

(7) An estimate of ϵ_1 and h_1 for CH_4^{2+} and CH_4 can be attempted. First, it is clear that h_1 can be kept constant (−19.88 au) for the entire series (CH_4^{8+} to CH_4). Second, remembering that $\epsilon_i = h_i + e_i$, and remembering that e_1 is the self-interaction of the $1s^2$ pair plus the interaction of one 1s electron with the remaining, we can use the e_1 available for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} to obtain extrapolated values of e_1 for CH_4^{2+} and CH_4. We obtain e_1 = 7.81 au for CH_2^+ and e_1 = 9.07 au for CH_4; in turn (since $\epsilon_1 = h_1 + e_1$) we obtain ϵ_1 = −12.07 au for CH_4^{2+} and ϵ_1 = −10.81 au for CH_4. The computed Hartree–Fock values are −12.04 au for CH_4^{2+} and −11.21 au for CH_4, respectively. This estimate is incorrect (96%) for CH_4 since the electron–electron repulsion e_1 for CH_4 was overestimated; the extrapolation does not include the fact that the distribution of the valency electron in the neutral molecule is more diffuse than in the ions (and, therefore, in CH_4 there is less repulsion between the 1s electrons and the valency electron than in the CH_4^{n+} ions).

Table III. ϕ_2 Bond Energy Analysis for Neutral and Ionized Methane (in au)

Energy	$C^{2+}(^1S)$	CH_4^{6+}	CH_4^{4+}	CH_4^{2+}	CH_4
h_2	−4.1194	−6.0836	−5.8670	−5.6596	−5.4629
h_2(C)	−4.1194	−4.9872	−4.7511	−3.7152	−2.4175
h_2(H)		0.0037	−0.0046	0.0024	−0.0048
h_2(CH)		−0.3524	−0.3641	−0.5134	−0.6666
h_2(HH)		−0.0037	−0.0040	−0.0031	−0.0124
h_2(CHH)		0.0558	−0.0600	0.0204	−0.0476
h_2(HHH)		−0.0035	−0.0034	0.0009	0.0001
e_2	2.4254	2.4551	3.3020	3.9755	4.5214
e_2(C)	2.4254	3.0690	3.6043	2.7999	1.7149
e_2(H)		−0.0000	0.0095	−0.0024	0.0028
e_2(CH)		−0.1659	0.0714	0.3099	0.5938
e_2(HH)		0.0000	0.0005	0.0016	0.0073
e_2(CHH)		−0.0008	0.0037	−0.0126	0.0658
e_2(HHH)		0.0001	0.0001	−0.0011	−0.0019
e_2(CHHH)		−0.0004	0.0000	−0.0018	−0.0072
e_2(HHHH)		−0.0000	0.0000	0.0003	0.0003
ϵ_2	−1.6941	−3.6285	−2.5649	−1.6840	−0.9415
ϵ_2(C)	−1.6941	−1.9182	−1.1468	−0.9152	−0.7026
ϵ_2(H)		0.0037	0.0050	0.0049	0.0023
ϵ_2(CH)		−0.5183	−0.4355	−0.2045	−0.0727
ϵ_2(HH)		−0.0037	0.0035	0.0015	−0.0051
ϵ_2(CHH)		0.0643	0.0563	0.0078	0.0182
ϵ_2(HHH)		−0.0035	−0.0033	−0.0002	−0.0018
ϵ_2(CHHH)		−0.0004	0.0000	−0.0018	−0.0072
ϵ_2(HHHH)		0.0000	0.0000	0.0003	0.0003

four-center contributions for CH_4^{6+}, CH_4^{4+}, CH_4^{2+}, and CH_4. The second orbital is mainly a 2s atomic orbital, with two variations: the electronic cloud is shifted toward the carbon nucleus and, at the same time, toward the four protons. Therefore, the electronic density is no longer spherically symmetrical. The two opposite shifts bring about a *pronounced* decrease in the 2s electronic density (relative to the distribution in the atom) in the region of the 2s function between the maximum and the protons, followed by an increase in the proximity of the protons. By inspection of Table III, we see that in CH_4^{6+} the *electronic* repulsion e_2(C) is larger than in the carbon ion C^{2+} (first variation). This increase is compensated by an electronic *attraction* e_2(CH) (second variation). By adding electrons to the system, the value of e_2(CH) becomes positive (CH_4^{4+}) and then increases sharply because of the interaction with the electrons around the protons (~0.3 au for CH_4^{2+} and ~0.6 au for CH_4).

The one-electron energy, h_2, decreases from CH_4^{6+} to CH_4. More specifically, from Table II we see that h_2(CH) is nearly constant for CH_4^{6+} and CH_4^{4+}. When we add electrons to the protons (CH_4^{2+} and CH_4), there is an increase of about 0.15 au for CH_4^{2+} and an additional increase of about 0.15 au for CH_4. If we keep in mind that there are four h_2(CH) terms, then we see that the *gradual* decrease of h_2 is achieved by *nongradual variations* in h_2(C) and h_2(CH).

We note that it has been "traditional" to report in the literature the orbital energies, ϵ, and to neglect the one-electron energies, h, as well as the electronic interaction, e. It is a pity since, by so doing, we emphasize a quantity which has more of a mathematical than physical value and we lose an opportunity to understand the physical picture embodied in the Hartree–Fock model.

Table IV. ϕ_3 Bond Energy Analysis for Neutral and Ionized Methane (in au)

Energy	CH_4^{4+}	CH_4^{2+}	CH_4
h_3	−5.5115	−5.1641	−4.8031
h_3(C)	−2.2447	−1.3720	−0.9423
h_3(H)	−0.0132	−0.0445	−0.0647
h_3(CH)	−0.7207	−0.8557	−0.8939
h_3(HH)	−0.0182	−0.0417	−0.0549
h_3(CHH)	−0.0392	−0.0013	0.0290
h_3(HHH)	0.0038	0.0168	0.0256
e_3	0.3019	3.8656	4.2855
e_3(C)	2.1151	1.2903	0.8057
e_3(H)	0.0016	0.0138	0.0362
e_3(CH)	0.0306	0.6080	0.7197
e_3(HH)	0.0011	0.0145	0.0428
e_3(CHH)	−0.0083	0.0029	0.0789
e_2(HHH)	0.0003	−0.0119	0.0326
e_3(CHHH)	−0.0005	−0.0151	−0.0367
e_3(HHHH)	0.0003	0.0044	0.0030
ϵ_3	−2.2096	−1.2985	−0.5446
ϵ_2(C)	−0.1296	−0.0817	−0.1366
ϵ_3(H)	−0.0116	−0.0307	−0.0285
ϵ_3(CH)	−0.4140	−0.2477	−0.1742
ϵ_3(HH)	−0.0171	−0.0272	−0.0121
ϵ_3(CHH)	−0.0475	0.0161	0.1079
ϵ_3(HHH)	0.0029	0.0049	−0.0070
ϵ_3(CHHH)	−0.0005	−0.0151	−0.0367
ϵ_3(HHHH)	0.0003	0.0044	0.0030

The Third Electron Pair. The relevant data for the triply degenerate third orbital are given in Table IV. Since we have reported data not only for CH_4^{4+}, but also for CH_4^{2+} and CH_4, the table contains the energy decomposition for the fourth and fifth orbital. For CH_4^{4+} we note that the total h_3(CH) contribution is 4 × (0.72) = 2.88 au; this value is larger than h_3(C) = 2.24 au. The electron–electron term, e_3, however, behaves oppositely: e_3(C) = 2.11 au and 4 × e(CH) = 0.12 au. These data are consistent with the interpretation that only a small electronic charge is at the protons in CH_4^+. (Clearly, this charge sharply increases for CH_4^{2+} and CH_4.) Whereas in the carbon atom the third orbital is a 2p, in CH_4^{4+} the third orbital extends itself away from the carbon by making use of the four

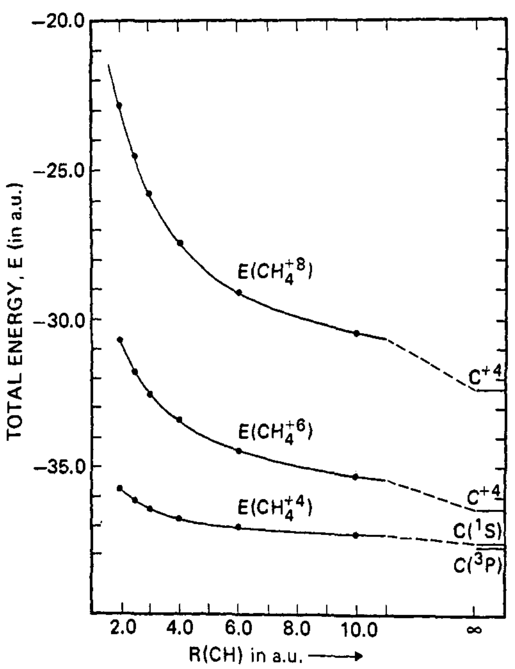

Figure 1. Variation of the total energy for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} with the C-H bond distances. The total energy and the R(C-H) distances are given in au. For infinite R(C-H) separation, the products are four protons and carbon ions in the ^1S state for CH_4^{8+} and CH_4^{6+}, to the carbon atom for CH_4^{4+}. In the figure we have reported both the energy of the carbon atom in the ^1S state and in the ^3P state (the Hartree-Fock model will lead to a singlet state and since we have not imposed spherical symmetry at R(CH) = ∞, the angular momentum of the dissociated atom will not be a good quantum number).

protons. More precisely, electronic charge is transferred to the protons. The phases of the corresponding functions at the protons (+1s or − 1s) are alternatively positive and negative, resulting in two protons with positive sign s-type functions and two protons with negative sign s-type functions around them. The 2p function arranges itself so as to be bonding (positive side of the 2p pointed toward the positive s-type distribution around two protons and negative side of the 2p pointed toward the negative s-type distribution around the two remaining protons).

Anticipating the analysis reported later in this paper, it is clear what will happen for CH_4^{2+} and CH_4. There are three 2p orbitals ($2p_x$, $2p_y$, and $2p_z$, or $2p_0$, $2p_{+1}$ and $2p_{-1}$) available for the carbon. Each of the three degenerate orbitals in CH_4 will have the basic distribution as described above: a 2p at the carbon's origin linked, in a bonding way, to the charges around two of the protons at one lobe of the 2p function and linked, also in a bonding way, to the charges around the remaining two protons at the opposite lobe of the 2p function. The charges around the protons need, therefore, to have positive signs for two of them, negative signs for the remaining two. *Such a distribution, clearly, is not restricted to be the sp^3 hybridization postulated in the valence bond approximation*: it does not require a pairing between one of the four sp^3 hybrids and one electron on the hydrogen.

However, let us remember that whereas *we* have used an orbital model, *the electrons* use an exact solution to the Schroedinger equation. Thus, we must stress that the valence bond hybridation model (sp^3) or the above molecular orbital model are only approximations and all that has some physics in it is the total density, rather than an orbital by orbital description. (On the other hand, in order to obtain a *simple mental model*, we have to refer to an orbital by orbital description.)

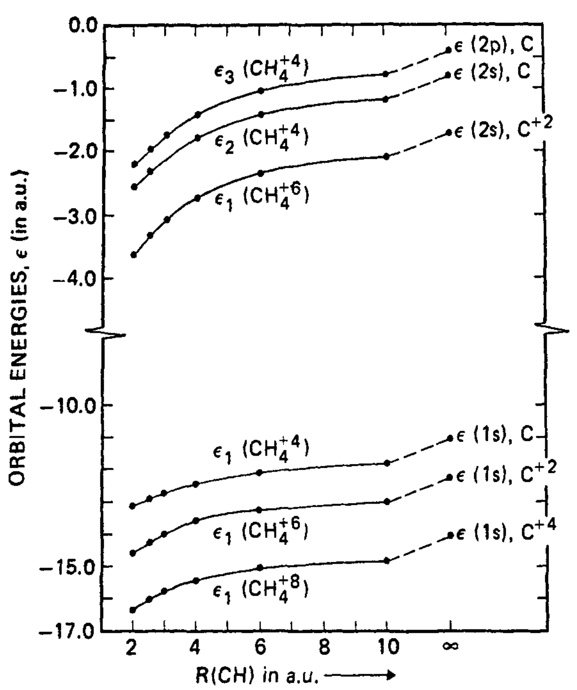

Figure 2. Variation of the orbital energies, E's, with the CH internuclear separation. As in Figure 1, the variation is constrained to the internuclear distance only, with constant value for the H-C-H angles.

In addition, one could notice that the orbital model we have presented is not unique; the density of our function is invariant under any unitary transformation. For example, one could prefer a description whereby a set of localization constraints are imposed on the density. We have chosen not to do so since (1) there is no basic reason to prefer one unitary transformation over another, and (2) the density as analyzed here is as directly obtained from the traditional Hartree-Fock method (and, therefore, molecular orbitals method).

Building Up of Methane. The First Six Electrons in the Field of Four Protons at Various Distances from the Carbon Nucleus

The only reason for having fixed the position of the proton at 2.0665 au from the carbon nucleus is that this is the experimental position for the neutral molecule, CH_4. From the simple model presented in the previous section, we know that the systems CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} are repulsive relative to C^{4+} and four protons, C^{2+} and four protons, and C and four protons, respectively. Let us now relax the geometrical constraint and follow the variation in the energy of the CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} systems when the protons are allowed to withdraw from the carbon ion or atom, respectively. Table V (and Figures 1 and 2) reports the main data. The results obtained are as expected: CH_4^{8+} is more repulsive than CH_4^{6+} and CH_4^{6+} is, in turn, more repulsive than CH_4^{4+}. The ions gradually go to the expected dissociation products which are obtained at large C-H distances, since Coulomb's law has a long range effect. (See Figure 1 and Table V.) The behavior of the total *electronic* energy,

Table V. Bond Energy Analysis for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} at Various C–H Distances (in au)

		R(CH)					
Case	Energies	2.0665	2.5	3.0	4.0	6.0	10.0
CH_4^{8+}	E	−22.8404	−24.4913	−25.8029	−27.4424	−29.0820	−30.3936
	E_e	−36.3919	−35.5610	−35.0277	−34.3610	−33.6943	−33.1610
	ϵ_1	−16.3525	−16.0168	−15.7502	−15.4168	−15.0835	−14.8168
	ϵ_1(C)	−14.4075	−14.4121	−14.4144	−14.4163	−14.4168	−14.4168
	ϵ_1(CH)	−0.4860	−0.3344	−0.4005	−0.2501	−0.1667	−0.1000
	h_1	−19.8798	−19.2775	−19.5442	−18.9442	−18.6109	−18.3441
	h_1(C)	−17.9314	−17.9377	−17.9409	−17.9435	−17.9442	−17.9441
	h_1(CH)	−0.4868	−0.3349	−0.4008	−0.2502	−0.1667	−0.1000
CH_4^{6+}	E	−30.7675	−31.7572	−32.5227	−33.4860	−34.4562	−35.2332
	E_e	−44.1594	−42.8239	−41.7474	−40.4045	−39.0686	−38.0006
	ϵ_1	−14.5713	−14.2591	−13.9925	−13.6522	−13.3200	−13.0542
	ϵ_1(C)	−12.2996	−12.1077	−12.2444	−12.5515	−12.6476	−12.6542
	ϵ_1(CH)	−0.5715	−0.5472	−0.4422	−0.2755	−0.1681	−0.1000
	h_1	−19.8760	−19.5404	−19.2737	−18.9403	−18.6070	−18.3403
	h_1(C)	−17.9231	−17.9310	−17.9354	−17.9393	−17.9403	−17.9403
	h_1(CH)	−0.4878	−0.4022	−0.3345	−0.2502	−0.1667	−0.0999
	ϵ_2	−3.6285	−3.3034	−3.0327	−2.6932	−2.3593	−2.0924
	ϵ_2(C)	−1.9182	−2.0535	−1.9908	−1.7865	−1.7003	−1.6924
	ϵ_2(CH)	−0.5183	−0.4272	−0.3330	−0.2407	−0.1654	−0.0999
	h_2	−6.0836	−5.7210	−5.4485	−5.1188	−4.7823	−4.5135
	h_2(C)	−4.9872	−5.5471	−5.2132	−4.4029	−4.1343	−4.1136
	h_2(CH)	−0.3524	−0.1232	−0.1117	−0.1918	−0.1627	−0.0999
CH_4^{4+}	E	−35.7559	−36.1725	−36.4363	−36.7204	−37.0003	−37.2382
	E_e	−49.1478	−47.2421	−45.6611	−43.6390	−41.6126	−40.0056
	ϵ_1	−13.1253	−12.9264	−12.7357	−12.4439	−12.0912	−11.8272
	ϵ_1(C)	−11.3939	−11.4145	−11.5661	−11.6469	−11.4709	−11.4416
	ϵ_1(CH)	−0.4301	−0.3672	−0.2896	−0.1984	−0.1551	−0.0964
	h_1	−19.8696	−19.5348	−19.2686	−18.9354	−18.6019	−18.3351
	h_1(C)	−17.9102	−17.9233	−17.9296	−17.9342	−17.9352	−17.9351
	h_1(CH)	−0.4893	−0.4027	−0.3346	−0.2503	−0.1667	−0.1000
	ϵ_2	−2.5649	−2.3045	−2.0759	−1.7673	−1.4296	−1.1701
	ϵ_2(C)	−1.1468	−1.1418	−1.0770	−0.9251	−0.8025	−0.7845
	ϵ_2(CH)	−0.4355	−0.3531	−0.2762	−0.2088	−0.1564	−0.0964
	h_2	−5.8670	−5.4748	−5.1831	−4.8573	−4.5366	−4.2719
	h_2(C)	−4.7511	−4.7554	−4.3277	−3.8274	−3.8620	−3.8710
	h_2(CH)	−0.3641	−0.2420	−0.2432	−0.2557	−0.1683	−0.1000
	ϵ_3	−2.2096	−1.9524	−1.7207	−1.3975	−1.0482	−0.7808
	ϵ_3(C)	−0.1296	−0.1413	−0.2301	−0.3556	−0.3636	−0.3608
	ϵ_3(CH)	−0.4140	−0.3612	−0.2997	−0.2200	−0.1577	−0.0936
	h_3	−5.5115	−5.0492	−4.6770	−4.2376	−3.9051	−3.6204
	h_3(C)	−2.2447	−2.2753	−2.3559	−2.6652	−3.0924	−3.1571
	h_3(CH)	−0.7207	−0.6153	−0.5135	−0.3509	−0.1895	−0.1042

E_e, is opposite; by increasing the C–H distances, E_e decreases (the system becomes less stable). However, the electronic energy, E_e, is not sufficient to compensate for the nuclear repulsion and, therefore, the total energy, E, remains unstable with respect to dissociation products.

The major terms in the ϵ's at R(CH) = 2.0665 are ϵ(C) and ϵ(CH). By progressively removing the protons, the ϵ(CH) part becomes less and less important, and at large distances the ϵ's of the CH_4 ions equal the ϵ's of the carbon ions or atom, respectively. (See Figure 2.) From Table V, we see that the ϵ_1(C) in CH_4^{8+} is nearly equal to ϵ_1 of C^{4+} *at all* R(CH) distances; however, in CH_4^{4+} the ϵ_1(C) approaches the value of ϵ_1 in C^{2+} at large R(CH). Since $\epsilon_1(C) = h_1(C) + e_1(C)$ and since h_1(C) is nearly constant for any R(CH), the increase in ϵ_1(C) is due to decrease in e_1 (of course, we remember that ϵ_1 is a positive quantity). The decrease in e_1 is due to the variation in the 2s electronic charge distribution, as discussed in the previous section (*via* the interaction terms between 1s and 2s).

In CH_4^{4+}, the ϵ_2(C) goes to a value of −0.7845 and ϵ_3(C) to a value of −0.3609 for R(CH) = 10. These correlate nicely with the ϵ_2 and ϵ_3 of the carbon atom in the ^1S state ($\epsilon_2(2s) = -0.7394$ and $\epsilon_3(2p) = -0.3098$) and not with the ϵ_2 and ϵ_3 of the carbon atom in the ^3P state ($\epsilon_2(2s) = -0.7056$ and $\epsilon_3(2p) = -0.4333$). At $R(CH) = \infty$ the Hartree–Fock model yields a singlet state of unspecified angular momentum. The above observation indicates that the singlet is predominantly an S state.

In Table VI, the electron population obtained from the Hartree–Fock computations is given.[8] As expected, the ϕ_1 is, nearly 100%, a 1s function. The small, but always present, 3d population is used both for polarization and for supplementing deficiencies in the 1s functions. For equivalent reasons there is a nonnegligible 3d population for ϕ_2. It is noted that the function ($3d_{xx} + 3d_{yy} + 3d_{zz}$) is exactly equivalent to a 3s function. However, other combinations of the above 3d and of the $3d_{xy}$, $3d_{xz}$, and $3d_{zz}$ functions are true 3d functions. Therefore, since the population denoted in Table VI is mainly (but not fully) of the $3d_{xx} + 3d_{yy} + 3d_{zz}$ type, one should add most of its contributions to the quantity s(C) in the ϕ_1 and ϕ_2. This is not the case for the ϕ_3 orbitals; this orbital

[8] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841, 2338, 2343 (1955).

Table VI. Electronic Population Analysis for CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} at Various C–H Distances

		CH_4^{6+}	CH_4^{6+}		CH_4^{4+}		
R(C–H)		ϕ_1	ϕ_1	ϕ_2	ϕ_1	ϕ_2	ϕ_3
2.0665	s(C)	2.0003	2.0010	2.1353	2.0013	2.1471	0.0
	p(C)	0.0	0.0	0.0	0.0	0.0	1.4363
	d(C)	−0.0011	−0.0021	0.0483	−0.0028	0.0286	0.0046
	s(H)	0.0001	0.0002	−0.0299	0.0002	−0.0223	0.1285
	p(H)	0.0001	0.0001	−0.0160	0.0001	−0.0216	0.0113
2.5	s(C)	2.0004	2.0013	2.2176	2.0017	2.1422	0.0
	p(C)	0.0	0.0	0.0	0.0	0.0	1.4483
	d(C)	−0.0009	−0.0019	0.1138	−0.0024	0.0594	0.0036
	s(H)	0.0	0.0001	−0.0515	0.0001	−0.0248	0.1299
	p(H)	0.0	0.0001	0.0313	0.0001	−0.0257	0.0141
3.0	s(C)	2.0009	2.0017	2.1710	2.0021	2.0696	0.0
	p(C)	0.0	0.0	0.0	0.0	0.0	1.4903
	d(C)	−0.0010	−0.0020	0.1018	−0.0025	0.0428	0.0018
	s(H)	0.0	0.0	−0.0391	0.0	0.0109	0.1085
	p(H)	0.0	0.0	−0.0291	0.0	−0.0172	0.0185
4.0	s(C)	2.0010	2.0020	2.0030	2.0050	2.0001	0.0
	p(C)	0.0	0.0	0.0	0.0	0.0	1.6524
	d(C)	−0.0011	−0.0021	0.0770	−0.0026	−0.0174	0.0003
	s(H)	0.0	0.0	0.0107	0.0	0.0037	0.0704
	p(H)	0.0	0.0	−0.0093	0.0	0.0006	0.0164
6.0	s(C)	2.0011	2.0022	1.8409	2.0027	2.0052	0.0
	p(C)	0.0	0.0	0.0	0.0	0.0	1.8597
	d(C)	−0.0011	−0.0022	0.1651	−0.0027	−0.0088	0.0
	s(H)	0.0	0.0	−0.0008	0.0	0.0007	0.0317
	p(H)	0.0	0.0	−0.0007	0.0	0.0004	0.0034
10.0	s(C)	2.0011	2.0021	1.8320	2.0027	2.0106	0.0
	p(C)	0.0	0.0	0.0	0.0	0.0	1.8631
	d(C)	−0.0011	−0.0021	0.1680	−0.0027	−0.0107	0.0
	s(H)	0.0	0.0	−0.0	0.0	0.0	0.0341
	p(H)	0.0	0.0	0.0	0.0	0.0	0.0001

(the deformed $2p_x^2$(C) orbital) has, as previously noted, a small population at the proton sites, which decreases slowly by pulling the protons away from the carbon. It is of interest to note that the 2p population on the protons (2p(H) describing the population associated with $2p_x$, and $2p_y$, and $2p_z$ functions centered at the protons) is about in a 1 to 1 ratio with the s population for ϕ_2, and 1 to 10 ratio for ϕ_3. We can rationalize this by assuming that the charges on ϕ_2 and ϕ_3 at the protons need to be polarized (hybridized) with the charges on the carbon. This polarization is achieved with 2p function *at the proton* in ϕ_2, since no 2p function at the carbon is used in ϕ_2, but it is achieved with 2p functions *at the carbon* (in ϕ_3) since these are predominant in the ϕ_3 orbital.

Hybridization of CH_4

The CH_4^{4+} ion contains in its highest orbital (designated as ϕ_3) *the mechanism for explaining the electronic structure of the neutral CH_4.* The physical model is that one of the three 2p orbitals (*e.g.*, $2p_x$) transfers part of its charge of two electrons to the protons, *so as to make a bond with all four protons.* This binding, as briefly noted previously, is accomplished by having 1s type electronic charges on the *four* protons with alternate signs, twice positive and twice negative. The two charges with positive phases bind with the positive lobe of $2p_x$; the two charges with negative phases bind with the negative lobe of $2p_x$. This is an example of "pseudo-2p" charges obtained by sign alternation on the 1s type charges at the proton sites. Thus, the $2p_x$ electrons of carbon extend themselves over the protons, not only by simply expanding their charge distribution, but also by transferring some of their charge to the protons. Alternatively, we can say that CH_4 has the electronic structure of C^{4-}, with polarization of the $2p_x^2$, $2p_y^2$, and $2p_z^2$ orbitals due to the four protonic charges.

There are three orbitals of 2p type: $2p_x$, $2p_y$, and $2p_z$; for each proton there are three possible connections to a second proton. Thus, there are three equivalent [H(+phase) H(+phase) 2p(C) H(−phase) H(−phase)] orbitals, all binding and, of course, degenerate.

For CH_4^{4+} one can use either $2p_x$ or $2p_y$ or $2p_z$; the three representations are equivalent. Alternatively, one can use a linear combination of them. We have selected to discuss CH_4^{4+} (and CH_4^{2+}) in terms of $2p_x$, because (a) we have used a single determinant, (b) the choice makes it easier to explain the model, and (c) it happens to conform with our Hartree–Fock computation. Since the carbon and the hydrogen atoms have nearly the same electronegativity, one would expect that the carbon atom will retain six electrons and each hydrogen atom will retain one electron in CH_4; *i.e.*, one would expect only a small charge transfer between H and C.

From this model, the overall binding of CH_4 is the result of a compromise between (a) stabilization of C^{4-} by adding protonic charges outside the nucleus and (b) screening of the protonic charges, so as to minimize their repulsion.

When the protons are at the nucleus, the electronic density is fully stabilized (being equal to the density of Ne(^{1}S); united atom). When the protons are infinitely separated, the electronic density is unstable and C^{4-} loses electrons to gain stability. When the protons are near the nucleus, the electronic density is stabilized by rearrangements (following polarization induced by the protons) which tend to preserve the united atom overall strucure.

The united atom structure can fully be exhibited only when the four protons are within the 1s shell of the carbon atom. Here the 1s electrons attain an orbital energy close to the one for the new atom and the remaining eight electrons have $2s^2\ 2p^6$ configuration.

At larger proton, carbon–nucleus distances, the 1s electrons will be progressively more and more carbon type 1s electrons (if we equate "type" with orbital energies values). Of the eight valency electrons, four will have $2s^2\ 2p^2$ distribution; the remaining four will have $2p^4$ distribution obtained by "pseudo-2p" arrangement.

Thus, by increasing (from zero) the R(C–H) distance, one goes from a $1s^2\ 2s^2\ 2p^6$ distribution to a $1s^2\ 2s^2\ 2p^2\ 2p_{\text{pseudo}}{}^4$ distribution, and finally to a $(1s^2\ 2s^2\ 2p^2)\ 1s^4$ distribution, where the set of $1s^4$ electrons are then around the 4 protons (hydrogen atoms).

This model brings about the following expected distribution for ϕ_2, ϕ_3, ϕ_4, and ϕ_5 in $CH_4{}^{4+}$, $CH_4{}^{2+}$, and CH_4

$CH_4{}^{4+}$

$$\phi_2 = 2s^{2.00}(C)$$

$$\phi_3 = 2p_x{}^{2.00}(C)$$

$CH_4{}^{2+}$

$$\phi_2 = 2s^{2.00}(C)$$

$$\phi_3 = 2p_{x\text{-pseudo}}{}^{1.00}(H)\ 2p_x{}^{1.00}(C) = 4 \times 1s^{0.25}(H)\ 2p_x{}^{1.00}(C)$$

$$\phi_4 = 2p_{y\text{-pseudo}}{}^{1.00}(H)\ 2p_y{}^{1.00}(C) = 4 \times 1s^{0.25}(H)\ 2p_y{}^{1.00}(C)$$

CH_4

$$\phi_2 = 2s^{2.00}(C)$$

$$\phi_3 = 2p_{x\text{-pseudo}}{}^{1.33}(H)\ 2p_x{}^{0.66}(C) = 4 \times 1s^{0.33}(H)\ 2p_x{}^{0.66}(C)$$

$$\phi_4 = 2p_{y\text{-pseudo}}{}^{1.33}(H)\ 2p_y{}^{0.66}(C) = 4 \times 1s^{0.33}(H)\ 2p_y{}^{0.66}(C)$$

$$\phi_5 = 2p_{z\text{-pseudo}}{}^{1.33}(H)\ 2p_z{}^{0.66}(C) = 4 \times 1s^{0.33}(H)\ 2p_z{}^{0.66}(C)$$

yielding s^2p^2 hybridization for $CH_4{}^{4+}$, $CH_4{}^{2+}$, and CH_4. Since the bonding of the carbons to the hydrogens is *via* 2p(C) and $2p_{\text{pseudo}}$(H), the binding can be expected to be increased by allowing the $\Phi(2)$ to transfer part of its 2s(C) charge to the 2p(C) distribution. In addition, since protons like electrons, one can expect the protons in $CH_4{}^{4+}$ to have a small amount of charge density (written either as 1s(H) or as $2p_{\text{pseudo}}$ (H)).

With this in mind, let us look at the Mulliken electron population analysis for the ϕ_3 to ϕ_5 orbitals in $CH_4{}^{4+}$, $CH_4{}^{2+}$, and CH_4. We have obtained the following charge distributions from the Hartree–Fock computations.

$CH_4{}^{4+}$

$$\phi_3 = 1s^{0.12}(H)\ 2p_x{}^{1.44}(C)$$

$CH_4{}^{2+}$

$$\phi_3 = 1s^{0.16}(H)\ 2p_x{}^{1.06}(C)$$

$$\phi_4 = 1s^{0.16}(H)\ 2p_y{}^{1.06}(C)$$

CH_4

$$\phi_3 = 1s^{0.28}(H)\ 2p_x{}^{0.86}(C)$$

$$\phi_4 = 1s^{0.28}(H)\ 2p_y{}^{0.86}(C)$$

$$\phi_5 = 1s^{0.28}(H)\ 2p_z{}^{0.86}(C)$$

The total s,p population in $CH_4{}^{4+}$, $CH_4{}^{2+}$, and CH_4 is $s^{2.14}\ p^{1.44}$ (for $CH_4{}^{4+}$); $s^{1.98}\ p^{2.11}$ (for $CH_4{}^{2+}$), and $s^{1.61}\ p^{2.57}$ (for CH_4). These values are subject to small corrections due to the introduction of polarization functions (as discussed later in this paper).

Thus, we conclude that the main hybridization is of s^2p^2 type, with corrections introduced mainly by the ϕ_2 orbital. These corrections are, however, in no way sufficient to shift the hybridization to the sp^3 type as demanded by the valency bond approximation. It is noted that the sp^3 hybridization is the result of a physical model which, from the onset, "assumes" that CH_4 is an eight-electron problem with sp^3 hybridization on the base of nonunique symmetry constraints for the molecule.

Table VII. Electronic Population by Basis Function's Type and Center (R(CH) = 2.0665 au)

	CH_4	$CH_4{}^{2+}$	$CH_4{}^{4+}$	$CH_4{}^{6+}$	$CH_4{}^{8+}$
s(C)	3.6083	3.9814	4.1484	4.1363	2.0003
p_x(C)	0.8568	1.0574	1.4363	0.0	0.0
p_y(C)	0.8568	1.0574	0.0	0.0	0.0
p_z(C)	0.8568	0.0	0.0	0.0	0.0
d_{xx}(C)	−0.0179	−0.0092	0.0154	0.0154	−0.0004
d_{xy}(C)	0.0071	0.0	0.0	0.0	0.0
d_{xz}(C)	0.0071	0.0062	0.0	0.0	0.0
d_{yy}(C)	−0.0179	−0.0092	0.0052	0.0154	−0.0004
d_{yz}(C)	0.0071	0.0062	0.0045	0.0	0.0
d_{zz}(C)	−0.0179	−0.0182	0.0051	0.0154	−0.0004
s(H)	0.9501	0.4728	0.1064	−0.0298	0.0001
p_x(H)	0.0045	−0.0012	−0.0099	−0.0053	0.0000[a]
p_y(H)	0.0045	−0.0012	−0.0002	−0.0053	0.0000[a]
p_z(H)	0.0045	0.0115	−0.0002	−0.0053	0.0000[a]

[a] Full value is 0.000025.

In Tables VII and VIII, the electron population analysis computed for CH_4 and its ions are given. Table VII reports the total population, whereas Table VIII reports an orbital by orbital decomposition. The polarization functions (2p for H and 3d for C) somewhat alter the previously given hybridization data. Table VIII reports, in addition, the gross charge on the carbon and hydrogen atoms. The computational numerical accuracy is, of course, in excess of four decimals; the physical reliability, however, is likely to be no more than ±0.05 of an electron. Thus, whereas the numerical computation would tell us that each hydrogen adds 0.04 of a charge to the carbon, the physical interpretation we would advance is that the hydrogen is nearly neutral.

Table VIII. Total Electronic Population by Centers and Orbitals (R(CH) = 2.0665 au)

	CH_4		CH_4^{2+}		CH_4^{4+}		CH_4^{6+}		CH_4^{8+}	
	C	H	C	H	C	H	C	H	C	H
ϕ_1	1.9983	0.0004	1.9984	0.0004	1.9985	0.0004	1.9990	0.0003	1.9992	0.0002
ϕ_2	1.5562	0.1109	1.9465	0.0134	2.1757	−0.0439	2.1836	−0.0459		
ϕ_3	0.8638	0.2809	1.0636	0.2341	1.4409	0.1398				
ϕ_4	0.8638	0.2809	1.0636	0.2341						
ϕ_5	0.8638	0.2809								
Total	6.1460	0.9634	6.07212	0.4820	5.6151	0.09621	4.1826	−0.0456	1.9992	0.0002

Table IX. Energy and Population Analysis for CH_4 as a Function of R(CH)

R(CH)	1.90	2.0665	2.25	2.50	2.75	3.00	3.50	4.00	6.00	10.0
ϵ_1	−11.1645	−11.2098	−11.2560	−11.3107	−11.3553	−11.3910	−11.4386	−11.4764	−11.4769	−11.3626
ϵ_2	−0.9799	−0.9415	−0.9039	−0.8604	−0.8255	−0.7988	−0.7669	−0.7628	−0.7801	−0.7237
ϵ_3	−0.5680	−0.5446	−0.5206	−0.4909	−0.4642	−0.4403	−0.3997	−0.3695	−0.3628	−0.3557
ϵ_4, ϵ_5	−0.5680	−0.5446	−0.5206	−0.4904	−0.4642	−0.4403	−0.3997	−0.3695	−0.2785	−0.2438
E	−40.1956	−40.2136	−40.1875	−40.1080	−40.0046	−39.8946	−39.6882	−39.5196	−39.1566	−39.0751
1-C	1.3552	1.3408	1.3292	1.3074	1.2670	1.2052	1.0231	0.7954	0.2797	0.0860
1-H	0.2182	0.2176	0.2168	0.2145	0.2109	0.2074	0.2025	0.1966	0.1574	0.1474
1	2.2278	2.2214	2.1965	2.1654	2.1104	2.0349	1.8332	1.5810	0.9092	0.6756
1 + 2	−2.4146	−2.0675	−1.7289	−1.3440	−1.0297	−0.7568	−0.3034	0.0221	0.5276	0.6135
1 + 2 + 3	0.0831	−0.0644	−0.1494	−0.1785	−0.1484	−0.0896	0.0546	0.1932	0.5324	0.6135
BE	−0.5070	−0.5250	−0.4989	−0.4194	−0.3160	−0.2060	0.0004	0.1689	0.5320	0.6135
S(H)	0.9398	0.9501	0.9585	0.9668	0.9725	0.9747	0.9710	0.9674	1.0084	0.9999
P(H)	0.0136	0.0134	0.0155	0.0200	0.0246	0.0283	0.0295	0.0230	0.0031	0.0000
S(C)	3.6575	3.6083	3.5695	3.5377	3.5390	3.5752	3.7028	3.8338	3.9965	4.0311
P(C)	2.5934	2.5703	2.5463	2.5088	2.4607	2.4132	2.3339	2.2472	1.9648	2.0005
D(C)	−0.0645	−0.0326	−0.0117	0.0065	0.0119	−0.0007	−0.0387	−0.0426	−0.0070	−0.0311
C^-	−0.1864	−0.1460	−0.1041	−0.0531	−0.0115	0.0122	0.0020	−0.0384	0.0457	−0.0005
H^+	0.0466	0.0365	0.0260	0.0133	0.0029	−0.0030	−0.0005	0.0096	−0.0014	0.0001

Ten Electrons in the Field of a Carbon Nucleus and Four Protons at Various Distances

The results of a series of computations and their analyses for the methane molecule using several C–H bond lengths, R(CH), and tetrahedral symmetry are reported in Table IX. The R(CH) values used are 1.9, 2.0665, 2.25, 2.5, 2.75, 3.0, 3.5, 4.0, 6.0, and 10.0 au. For each geometry, the orbital energies ϵ_1, ϵ_2, ϵ_3, and ϵ_4, ϵ_5 (ϵ_4 and ϵ_5 are degenerate with ϵ_3 for intermediate values of R(CH)), the total energy E_1 and the Hartree–Fock binding energy BE are given. The latter quantity is defined as the energy difference between E and the Hartree–Fock energy of C(^{3}P) plus four times the Hartree–Fock energy of H(^{2}S). Also given are the one-center energy for the carbon atom (*i.e.*, $\Sigma_{i=1}^5 h_i(C) + \Sigma^5 \epsilon_i(C)$), the one-center energy for the hydrogen atom (*i.e.*, $\Sigma_{i=1}^5 h_i(H) + \Sigma_{i=1}^5 \epsilon(H)$), and and the sum of the C one-center energy plus four times the H one-center energy. These quantities are designated by 1-C, 1-H, and 1, respectively. 1-C is measured relative to the C(^{3}P) Hartree–Fock energy (−37.6886 au) and 1-H relative to the H(^{2}S) Hartree–Fock energy (−0.5000 au). In addition, the sum of the one- and two-center contributions (designated by 1 + 2) and the sum of the one-, two-, and three-center contributions (designated by 1 + 2 + 3) to BE are reported. The values of the various contributions to BE are plotted in Figure 3 as a function of R(CH). The curve labeled 1 + 2 + 3 + 4 corresponds to a plot of the binding energy since BE is equal to the sum of one-, two-, three-, and four-center contributions.

The remaining data of Table IX are the s and p electronic populations of the H atoms, the s, p, and d populations of the C atom, and the total ionic character of C and H obtained from a population analysis of the Hartree–Fock wave functions. The Hartree–Fock model breaks down at large distances (with the exception of cases where the molecular orbitals can clearly be separated into subsets at large distances, each subset correctly describing a separated atom). For methane, it is well known that there is no way to assign one orbital to a single hydrogen using a single determinant. The bond energy analysis indicates an additional feature of the Hartree–Fock model. As discussed in the previous paper[6] of this series, the one-center energies can be equated with the energy of the valency states of the component atoms in the molecule. This type of a valency state has been designated the "molecular orbital valency state" (MOVS). It is evident from Figure 3 and from Table VIII that the breakdown at large distances is the result of a poor MOVS choice, especially for the H atoms, forced on the traditional Hartree–Fock model. However, this poor MOVS choice remains at all distances (not only large distances) and requires a very efficient binding mechanism to overcome this initial error. The various energy contributions resulting from the bond energy analysis are smoothly varying functions and *there is no sudden "breakdown" in going from intermediate to large values of R(CH)*. The only irregular feature is introduced by comparing the Hartree–Fock binding with the Hartree–Fock atomic dissociation products. Despite the rather fundamental nature of the questions raised here, we shall not discuss the overall validity of the Hartree–Fock model in molecular computations. We wish only to stress that (a) binding is obtained, rel-

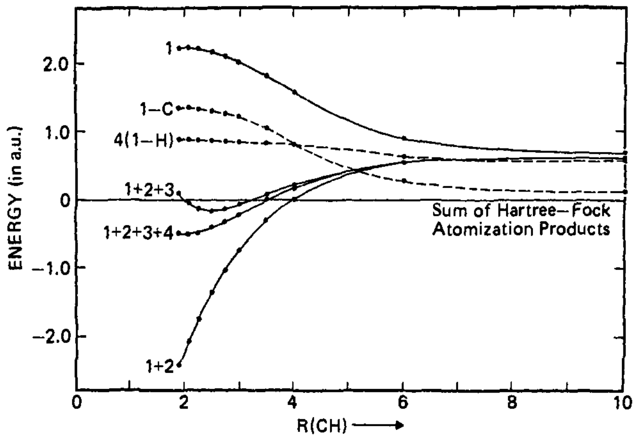

Figure 3. Decomposition of the total energy in atomic centers components. The curve labeled 1 is the sum of the one-center energy for the carbon (labeled 1-C) and of the one-center energies for the four hydrogen atoms (labeled 4(1-H)). The one center for the carbon atom nearly goes to the ^3P value for large C–H distances. The energy of the four hydrogens does not dissociate properly (as discussed with text). The one-center energy for the carbon and the hydrogens does not give binding; when the two-center energies are added (curve 1 + 2) there is binding up to about R(C–H) = 4.0 au; the inclusion of the three-center energy (curve 1 + 2 + 3) produces a minimum at a R(C–H) shorter than the experimental. The minimum is then shifted to nearly the experimental value when the four-center energy is added (curve 1 + 2 + 3 + 4). By definition, the latter curve coincides with the computed total potential energy of CH_4, for different R(CH) distances.

ative to the separated Hartree–Fock atoms, by a very large cancellation of the various terms (resulting from a bond energy analysis); (b) there is no irregularity in the terms but rather a smooth variation, making it questionable to talk of a "breakdown of the model;" and (c) the above energy decomposition by centers is basis set dependent, *but its overall picture is not*, as can be seen by comparing the data in Table VIII with those reported in a previous paper of this series obtained by using a quite different (and inferior) basis set.[6]

Single-Electron Ionization

In this section, we comment on the vertical ionization potentials, obtained by ejecting a single electron from either ϕ_1 or ϕ_2 or one of the three degenerate orbitals, ϕ_3, ϕ_4, and ϕ_5. The Frank–Condon factor is expected to be unity for the $\phi_1^2 \rightarrow \phi_1^1$ ionization, but smaller for $\phi_2^2 \rightarrow \phi_2^1$ and $\phi_3^2 \rightarrow \phi_3^1$. (As known, CH_4^+ of configuration $\phi_1^2\ \phi_2^2\ \phi_3^1\ \phi_4^2\ \phi_5^2$ does not have tetrahedral geometry.) Thus, the data obtained from this section should not be compared with adiabatic ionization potential but only with the vertical ionization potentials.

Ejecting one electron from CH_4 brings about a CH_4^+ ion; the question of importance for understanding the electronic structure of the ion is the *magnitude of the electronic density rearrangement* which follows the ionization. In general, one would expect a considerable rearrangement since the field of a negative charge is substituted with the field of a positive hole. In addition, one would expect a rearrangement which reflects the specific nature of the orbital from which the electron is ejected. Therefore, the question we shall ask is the following. Given an excitation of an electron from the orbital ϕ_i (i = 1, 5) and knowing from the preceding sections of this paper the nature of ϕ_i, how will the electrons rearrange themselves in ϕ_1, ϕ_{i-1}, ϕ_{i+1}, ... after ionization? In particular, how much charge will be transferred from the hydrogens to the carbons, and what is the value of the charges q and q', where q and q' are defined by the notation $C^q(H^{q'})_4$, describing CH_4^+ (namely, are the excess charges, either positive or negative, relative to the charge for the neutral atoms). A second question is as follows. Is the effect of the hole spread uniformly in the atom or localized in a few orbitals?

Let us start by considering the ionization $\phi_1^2 \rightarrow \phi_1^1$. The main effect is the loss of a 1s electron from "the carbon atom in the methane molecule." Due to the small overlap between the 1s and remaining electrons, we can say that the remaining electrons will be rather uniformly attracted toward the carbon nucleus. Thus, we expect an H → C charge transfer. The ϕ_2 orbital (1.55 e on carbon and 0.45 e on the four hydrogens in CH_4 neutral) will tend to shift the electronic charges it had on the hydrogens to the carbon. The three degenerate orbitals (with a total charge of 2.59 e at the carbon and 0.85 at each hydrogen) will attempt to do the same, but somewhat less efficiently, since now the hole has been somewhat screened by the charges transferred from the hydrogens to the carbon in ϕ_2. The quantitative amount of charge transfer per orbital is given in Table X. There is a charge transfer of 0.30 e in ϕ_2 and a charge transfer of 0.28 e from the four hydrogens in each of the three degenerate orbitals, more than compensating for the one electron lost in the 1s of the carbon.[9] The total charge on the carbon and hydrogens varies as a function of the hydrogen–carbon distance. It *increases* at the carbon center by increasing the distances *but only slightly*, and the variation is likely smaller than the electronic population analysis "physical" accuracy.

Let us now ionize an electron in the CH_4 molecule out of the second orbital ($\phi_2^2 \rightarrow \phi_2^1$ process). The positive hole created is much more diffuse than in the $\phi_1^2 \rightarrow \phi_1^1$ process and partly extends over the protons. Thus, we would expect much less H → C charge transfer than in the $\phi_1^2 \rightarrow \phi_1^1$ process. In detail ϕ_1 will remain as it was in neutral CH_4; part of the charges on the hydrogen in ϕ_2 will be transferred to the "carbon" atom, but not all, because of the spread of the ϕ_2 hole at the protons; for the same reason, the H → C charge transfer from ϕ_3, ϕ_4, ϕ_5 will be less efficient than in the $\phi_1^2 \rightarrow \phi_1^1$ process. Table X tells us that the ion has the structure $C^{+0.41}(H^{+0.15})_4$ to be compared with $C^{-0.31}(H^{+0.33})_4$ in CH_4^+ obtained from the $\phi_1^2 \rightarrow \phi_1^1$ process.

We now ionize one electron out of the three degenerate orbitals and indicate the process as $\phi_3^2 \rightarrow \phi_3^1$. The positive hole now has substantial density at the protons and, therefore, one will expect very little charge transfer in the three degenerate orbitals, relative to the distribution of these orbitals in the neutral CH_4. By removing 0.2 of an electron from each center in the total population of the three degenerate orbitals we would expect (at R(CH) = 2.0665 au) 2.59 − 0.2 =

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[9] From Table X, it appears that the loss of the one 1s electron from ϕ_1 in CH_4^+ is followed by a rearrangement which affects more the hydrogens than the carbon (the total population at the carbon is now ~6.3 e, whereas the total population at the hydrogen is now ~0.67 e, compared to 6.18 and 0.95 e in CH_4). Thus, the pseudo-2p electrons are those which are affected more.

Table X. Electronic Population Analysis for CH_4 and CH_4^+

	CH_4		CH_4^+ (ϕ_1)		CH_4^+ (ϕ_2)		CH_4^+ (ϕ_3)		R(CH), au
	C	H	C	H	C	H	C	H	
ϕ_1	1.9977	0.0006	0.9993	0.0002	1.9975	0.0006	1.9977	0.0006	
ϕ_2	1.5719	0.0170	1.8488	0.0378	0.9054	0.0236	1.7778	0.0555	1.90
$\phi_3 + \phi_4 + \phi_5$	2.6167	0.8458	3.427	0.6393	2.6942	0.8265	2.3097	0.6726	
Total	6.1863	0.9534	6.2908	0.6773	5.5971	0.8507	6.0852	0.7287	
ϕ_1	1.9983	0.0004	0.9997	0.0001	1.9982	0.0004	1.9983	0.0004	
ϕ_2	1.5562	0.1110	1.8641	0.0340	0.9070	0.0233	1.7628	0.0593	2.0665
$\phi_3 + \phi_4 + \phi_5$	2.5915	0.8520	3.4486	0.6378	2.6806	0.8299	2.2924	0.6769	
Total	6.1460	0.9635	6.3124	0.6719	5.5858	0.8536	6.0535	0.7366	
ϕ_1	1.9988	0.0003	0.9999	0.0000	1.9988	0.0003	1.9988	0.0003	
ϕ_2	1.5398	0.1150	1.8606	0.0348	0.9015	0.0246	1.7355	0.0661	2.25
$\phi_3 + \phi_4 + \phi_5$	2.5655	0.8586	3.4708	0.6323	2.6878	0.8281	2.2913	0.6772	
Total	6.1041	0.9740	6.3314	0.6672	5.5880	0.8530	6.0257	0.7436	

Table XI. Orbital and Total Energies for CH_4 and CH_4^+

	CH_4	CH_4^+ (ϕ_1)	CH_4^+ (ϕ_2)	CH_4^+ (ϕ_3)	R(CH), au
ϵ_1	−11.1645	−13.7484	−11.6218	−11.5784	
ϵ_2	−0.9799	−1.4692	−1.4343	−1.3508	
ϵ_3	−0.5680	−1.0280	−0.9436	−1.0111	1.90
ϵ_4, ϵ_5	−0.5680	−1.0280	−0.9436	−0.9454	
E	−40.1956	−29.5359	−39.2667	−39.6729	
ϵ_1	−11.2098	−13.7627	−11.6439	−11.5952	
ϵ_2	−0.9415	−1.4061	−1.3782	−1.2945	
ϵ_3	−0.5446	−0.9748	−0.9023	−0.9633	2.0665
ϵ_4, ϵ_5	−0.5446	−0.9748	−0.9023	−0.9014	
E	−40.2136	−29.5239	−39.3234	−39.7124	
ϵ_1	−11.2560	−13.7732	−11.6670	−11.6132	
ϵ_2	−0.9039	−1.3440	−1.3234	−1.2389	
ϵ_3	−0.5206	−0.9214	−0.8607	−0.9155	2.25
ϵ_4, ϵ_5	−0.5206	−0.9214	−0.8607	−0.8572	
E	−40.1875	−29.4687	−39.3361	−39.7083	

Table XII. Vertical Ionization Potentials for CH_4

	Vertical IP (eV)	
Case	Computed	Exptl
CH_4	0.0	0.0
CH_4^+ (ϕ_3)	13.64	13.6[a] 13.77 ± 0.05[b]
CH_4^+ (ϕ_2)	24.22	23.1[a]
CH_4^{2+} (ϕ_1)	290.88	290.7 ± 0.3[a,c]
CH_4^{2+} (ϕ_3^2)	38.80	
CH_4^{2+} ($\phi_3\phi_4$) triplet	36.32	
CH_4^{2+} ($\phi_3\phi_4$) singlet	39.11	

[a] K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, *Chem. Phys. Lett.*, **1**, 613 (1968). [b] R. Stockbauer and M. G. Inghram, *J. Chem. Phys.*, **54**, 2242 (1971). [c] The experimental error of ±0.3 eV was obtained from a private communication from Dr. U. Gelius.

2.39 charges on the carbon and 0.85 − 0.2 = 0.65 charges on each hydrogen. The computed charges (Table X) for the carbon in ($\phi_3 + \phi_4 + \phi_5$) is 2.29 and for each hydrogen 0.68. The CH_4^+ electronic structure for the process $\phi_3^2 \rightarrow \phi_1^3$ (allowing for electronic charge reorganization, but not for geometrical reorganization of the nuclei) is $C^{-0.05}$ $(H^{+0.26})_4$.

To conclude this part of the analysis, it appears that one can easily understand the charge rearrangement, following ionization, by knowledge of the orbitals composing the function for the neutral molecule.

In Table XI, the computed total energies and orbital energies for the three CH_4^+ ions are given at R(C–H) = 1.9, 2.0665, and 2.25 au. From this table, the computed ionization potentials (see Table XII) are 13.64, 24.22, and 290.88 eV, respectively.

From Table XII, we learn that the computed vertical ionization potentials, when one properly uses the Hartree–Fock model, are in good agreement with experimental data in the CH_4 molecule. For the vertical ionization potential in $CH_4(\phi_1)$ and $CH_4(\phi_3)$ the agreement is within experimental error. For the case of $CH_4(\phi_2)$ the agreement is within ~1 eV of the experimental data (no error limit on the experimental value is given for this case). *As indicated in the previous paper of this series,*[6] *these conclusions are at "variance with those reached by other workers."*[10]

It is of interest to note that there seems to be no great need for the determination of the vertical ionization potentials in CH_4 to perform computations with inclusions of correlation corrections. Clearly, the corrections can only uniformly lower the total energy of both CH_4 neutral and positive ions. This brings about the question: How can this be the case, if there is one less pair in the ion than in the neutral molecule? We note that the correlation correction, being a function of the electronic density, will be dependent on the rearrangement of the electronic density, following ionization. The amount of the rearrangement cannot be estimated only on the base of the *reorganization energy, i.e.*, the difference between the vertical ionization potential as given in Table XII and the vertical ionization potential as given by making use of the orbital energies of the neutral molecule. Different densities of distribution can have *the same* Hartree–Fock energy and *different* correlation energies, since the density dependency of the two quantities is not the same one.

Another factor is that in comparing Hartree–Fock total energy of an open shell (the CH_4^+ ion, for example) with the Hartree–Fock energy of a closed shell (the CH_4 molecule, for example), one makes use of two different physical models, despite the use of the same formalism (and name for the model). In the closed-shell configuration, the orbital factor of the two spin orbitals belonging to the same molecular orbital are constrained to be *the same;* in an open-shell configuration this constraint does not apply for the orbital which has single occupancy. Thus, for

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(10) K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, *Chem. Phys. Lett.*, **1**, 613 (1968).

Table XIII. Orbital Exponents and Angular Factors for the Uncontracted Gaussian Set of Functions[a]

No.	Type	Exponent	Center
1	s	51731.61	C
2	s	5901.797	C
3	s	1158.752	C
4	s	313.5176	C
5	s	35.25698	C
6	s	32.05127	C
7	s	11.96647	C
8	s	4.897021	C
9	s	2.156893	C
10	s	0.671757	C
11	s	0.263095	C
12	s	0.104166	C
13, 20, 27	x, y, z	32.48146	C
14, 21, 28	x, y, z	7.334475	C
15, 22, 29	x, y, z	2.276541	C
16, 23, 30	x, y, z	0.841801	C
17, 24, 31	x, y, z	0.336374	C
18, 25, 32	x, y, z	0.143589	C
19, 26, 33	x, y, z	0.063619	C
24, 35, 36	xx, yy, zz	1.00000	C
37, 38, 39	xy, xz, yz	1.00000	C
40	s	68.1600	H(1)
41	s	10.2465	H(1)
42	s	2.34648	H(1)
43	s	0.67332	H(1)
44	s	0.22466	H(1)
45	s	0.082217	H(1)
46, 48, 50	x, y, z	1.000	H(1)
47, 49, 51	x, y, z	0.2000	H(1)

[a] For H(2), H(3), and H(4) we have used a basis set equal to the one above reported for H(1), bringing the total of uncontracted Gaussian's to 87 functions.

Table XIV. Contraction Coefficients Used in Forming the Linear Combination of Function for the Gaussian Given in Table XIII

Gaussians[a]	Expansion coefficients[a]	No.'s
1, 2, 3, 4, 5, 6:	0.002983, 0.033016, 0.192228, 0.836137, 0.269517, 0.769384	1
7:	1.0	2
8:	1.0	3
9:	1.0	4
10:	1.0	5
11, 12:	0.72681, 0.30458	6
13, 14, 15:	0.035018, 0.230874, 0.821107	7
20, 21, 22:	0.035018, 0.230874, 0.821107	8
27, 28, 29:	0.035018, 0.230874, 0.821107	9
16:	1.0	10
23:	1.0	11
30:	1.0	12
17:	1.0	13
24:	1.0	14
31:	1.0	15
18, 19:	0.810521, 0.221777	16
25, 26:	0.810521, 0.221777	17
32, 33:	0.810521, 0.221777	18
34:	1.0	19
35:	1.0	20
36:	1.0	21
37:	1.0	22
38:	1.0	23
39:	1.0	24
40, 41, 42:	0.002549, 0.01938, 0.09276	25
43:	1.0	26
44, 45:	0.492211, 0.2426	27
46:	1.0	28
47:	1.0	29
48:	1.0	30
49:	1.0	31
50:	1.0	32
51:	1.0	33

[a] The numbers preceding the colon identify the Gaussian given in Table XIII; the number following the colon is the expansion coefficient for the Gaussians. The number at the right of the table is a running number. A total of 69 functions is used.

an ion one of the constraints (which introduce the correlation errors) is removed at least for one electron.[11]

Conclusions

In this work we have not given reference to the previous numerous computations on CH_4. Reference to about 50 previous computations for CH_4 is available from the new and excellent bibliography by Richards, Walker, and Hinkley.[12]

From this work we can conclude that, by using Hartree-Fock atomic data, a great deal of information concerning the CH_4^{8+}, CH_4^{6+}, and CH_4^{4+} can be predicted in good agreement with Hartree-Fock computations. Since CH_4^{4+} contains one of the three degenerate orbitals, a reasonably accurate discussion on hybridization for CH_4 can be predicted, without performing computation. Finally, the charge transfer following the ionization of one electron can be explained from knowledge of the atomic populations. In brief, we have shown that the Hartree-Fock model corresponds to a *simple*, *understandable*, and to some extent, *numerically predictable* physical picture of the electron in the molecule. This physical picture is at variance with the one obtained from the valency bond method.

Hopefully, in time, we shall be in a position to generalize the simple physical model here presented to more complicated functions than the Hartree-Fock function.

Acknowledgment. We would like to express our sincere gratitude to two referees for their very useful work in finding misprints and inconsistency, as well as pointing out where the original manuscript was in need of clarification.

Appendix

The basis set used in these computations is a Gaussian type set and is reported in Tables XIII and XIV. Table XIII gives the orbital exponents of the Gaussian functions as well as the angular specifications. Table XIV reports the contraction coefficients used to form linear combinations of Gaussian function. The contracted functions, thus obtained, are the analytical basis on which the self-consistent field technique is applied. The basis set of this paper has been obtained by Dr. F. van Duijenevelt during his stay at our laboratory.

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(11) For an equivalent reason to the one here given, it is not simple to obtain simple rules for the estimate of the correlation energy in excited states, even for an even electron number system. Again, for the equivalent reason, attempts to estimate the correlation error in open-shell ground states for molecules have been less successful than attempts to estimate the correlation error for closed-shell ground state molecules.

(12) W. G. Richards, T. E. H. Walker, and R. K. Hinkley, "A Bibliography of *ab initio* Molecular Wave Functions," Clarendon Press, Oxford, 1971.